

FACILITY FORM 602

N 65 89753

(ACCESSION NUMBER)

13

(PAGES)

CR 67680

(NASA CR OR TMX OR AD NUMBER)

(THRU)

None

(CODE)

(CATEGORY)

MELPAR  INC

A SUBSIDIARY OF WESTINGHOUSE AIR BRAKE COMPANY

3000 ARLINGTON BOULEVARD

FALLS CHURCH, VIRGINIA

[STUDY IN COMETARY
ASTROPHYSICS]

First Quarterly Status Report

15 April 1964 to 15 June 1964

Contract No. NASw-890

for

National Aeronautics and Space
Administration
Washington, D. C.

Prepared by

Louis J. Stief & Vincent J. DeCarlo
Melpar, Inc.
3000 Arlington Boulevard
Falls Church, Virginia

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	2
2. PHOTOLYSIS OF ACETYLENE	3
2.1 Introduction	3
2.2 Results	4
2.3 Discussion	7
3. PHOTOLYSIS OF GASEOUS MIXTURES	8
3.1 Introduction	8
3.2 Results	8
3.3 Discussion	9
4. FUTURE WORK	10

1. INTRODUCTION

Research this quarter has put emphasis on the vacuum ultraviolet photolysis of acetylene and on the production of the CN violet system in emission in photolysis of gaseous mixtures. In the photolysis of acetylene, the effect of pressure and the wavelength of the exciting radiation on the intensity and spectral distribution of the observed emission and on the production of hydrogen has been examined quantitatively. The absolute intensity of the lamps has been measured and determinations of the quantum yield for hydrogen production are in progress.

The violet system of the CN radical has been observed in emission in the vacuum ultraviolet photolysis of the following gases: acetylene plus ammonia, acetylene plus nitric oxide and carbon dioxide plus nitric oxide.

Photolysis of methyl acetylene has been examined as a possible source for C_3 emission, but no emission was observed in the region 2000\AA - 7000\AA . Negative results were also obtained with CO and CO_2 .

Some changes in dimensions and construction of the vacuum UV resonance lamps have resulted in an increase in intensity by a factor of ten. This has enabled the production of the emission from methane with sufficient intensity to be recorded using a monochromator rather than filter combinations to estimate the spectral range. The observed emission extends from about 4500\AA to 6000\AA for methane at 50μ and is indistinguishable from the weak emission observed from acetylene at a pressure of 1 mm Hg.

An investigation has been initiated involving the photolysis of water vapor in the first continuum (1650\AA) with purpose of studying the reactions of OH radicals in the gas phase and in low temperature solids.

The initial experiments are being directed towards an elucidation of the primary process or processes involved in the photolysis of pure water vapor at 1650\AA° .

Some effort has been expended in an attempt to detect and record the absorption spectra of transient, reactive species produced in the photolysis of low temperature solids. A system is being developed using CS_2 as a source of the stable free radical CS to determine whether sufficient concentrations of the radical can be obtained in a thin, glassy, transparent deposit subsequent to a single flash of ultraviolet light. Results so far have shown that, although the absorption spectra of the parent compound is observed, no new absorptions are evident after photolysis under present conditions. Perfection of this technique would enable a study to be made at low temperatures of non-emitting transient species by means of their absorption spectra. Radicals of immediate interest are OH and HO_2 from the photolysis of H_2O_2 .

An apparatus is presently under construction for an investigation of the bombardment of low temperature solids with electrons. In addition, experimental designs have been developed for low temperature proton bombardment experiments.

2. PHOTOLYSIS OF ACETYLENE

2.1 Introduction

The vacuum ultraviolet photolysis of acetylene has continued in this quarter and it is expected that this activity will be completed by the end of the next quarter. The reaction cell, monochromator, lamps, etc. were described in reports for Contract NASw-589. Photolysis at the Kr (1236\AA°) and Xe (1465\AA°) resonance lines was employed.

2.2 Results

The emission observed subsequent to the photolysis of 50μ of acetylene vapor at $1236\overset{\circ}{\text{\AA}}$ still shows no structure under the improved resolution (1 mm slits, $64\overset{\circ}{\text{\AA}}/\text{m}$ dispersion) possible with more intense lamps. A broad, structureless emission in the region $4000\overset{\circ}{\text{\AA}}-6500\overset{\circ}{\text{\AA}}$ as shown in figure I of final report for NASw-589 is observed. No further attempt is contemplated to obtain a more detailed emission spectra. The emission observed in the photolysis of C_2D_2 is indistinguishable under our experimental conditions from that observed with C_2H_2 . Photolysis of acetylene at 56μ with Xe lamps of increased intensity has resulted in the observation of weak emission (about 10% of that observed with Kr lamp when corrected for intensity differences in lamps).

The effect of adding N_2 , O_2 or C_2H_2 on the intensity of the emission recorded in the photolysis of acetylene vapor at 56μ with $1236\overset{\circ}{\text{\AA}}$ light is shown in figure I.

Considerable effort has been expended on a study of the production of hydrogen in the photolysis of acetylene. In the pressure region of 50μ Hg (where the intensity of the emission is greatest), photolysis of C_2D_2 results in formation of comparable amounts of H_2 , HD and D_2 . This probably results from presence of water vapor which is subsequently photolyzed and/or exchanges with the deuterated acetylene. The effect is much less evident at higher pressures of acetylene (less H_2 formed, little or no HD). This indicates that water is not a significant contaminant in the acetylene before introduction into the cell since an increase in pressure at constant composition would not lead to increased absorption by C_2D_2 and increased production of D_2 relative to H_2 .

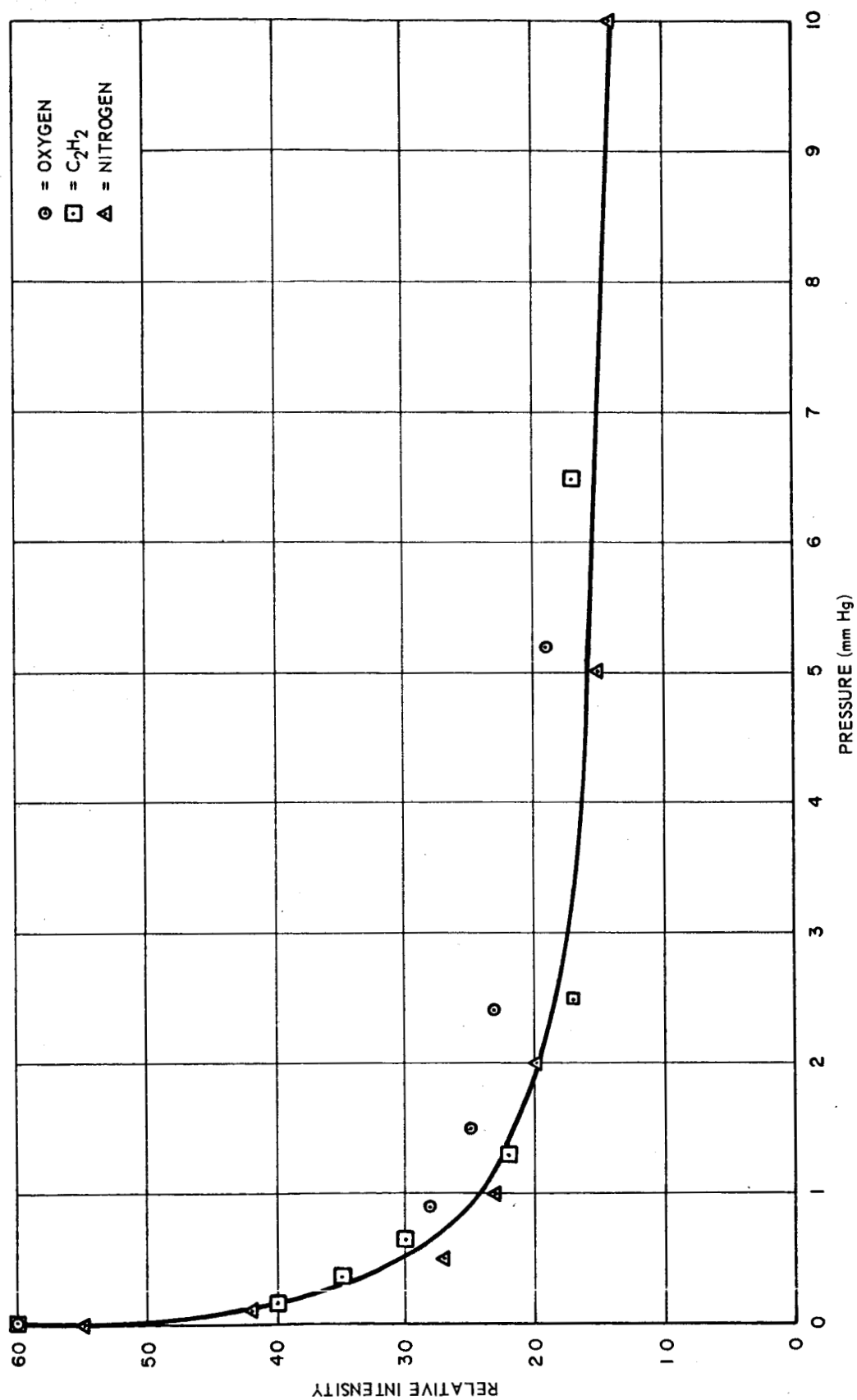


Figure 1. Effect of Pressure on the Intensity of Emission Produced in Photolysis of C₂H₂ at 1236 Å

Prolonged heating of the cell with continued evacuation to 10^{-6} mm Hg prior to photolysis failed to make a significant reduction in the amount of H_2 formed in the photolysis of C_2D_2 . This effect makes it impossible to obtain meaningful data from the photolysis of C_2H_2 - C_2D_2 mixtures.

In view of this, all results on the production of hydrogen from acetylene are based on the measurement of D_2 from the photolysis of C_2D_2 . This gives a minimum value for hydrogen production. Quantum yields are based on intensity measurements using CO_2 as an actinometer. CO_2 is photolyzed in the same cell used for the acetylene photolysis and intensity measurements are made immediately before and immediately after photolysis of the acetylene sample. CO formed in the photolysis of CO_2 is measured, a quantum yield of unity for CO production having been previously established.^{1,2} Plots of CO from CO_2 and hydrogen from C_2D_2 at 56μ are linear with time and reproducible to better than 5%. Results of measurements at 56μ and 2.4 mm Hg for photolysis of C_2D_2 at Kr line and for photolysis of 56μ C_2D_2 at Xe line are shown in table I along with the absolute intensities of the lamps.

Table I

Hydrogen Production in the Photolysis of Acetylene

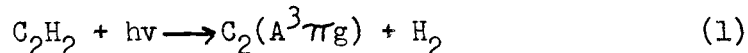
	Kr (1236Å)		Xe (1465Å)
	56 μ Hg	2.4 mm Hg	56 μ Hg
Pressure of acetylene			
% of light absorbed by acetylene	10%	100%	18%
Quantum yield (molecules/quanta) of D_2 from C_2D_2	0.064	≈ 0.006	0.052
Intensity of lamp (quanta/sec)	3.8×10^{15}	3.8×10^{15}	2.7×10^{15}

1. B. H. Mahan, J. Chem. Phys. 33, 959 (1960).
2. P. Warneck, Far. Soc. Discussion on Chemical Reactions in the Atmosphere, Edinburgh, April 1964.

For the 2.4 mm Hg experiment, the rate of hydrogen production is taken from the initial slope since polymer formation causes decreased absorption of light and hence decreased production of hydrogen with photolysis time. Corrections were made for % D₂ in the hydrogen from C₂D₂ and for fraction of incident light absorbed by CO₂ and C₂D₂ respectively based on absorption coefficients at 1236⁰Å and 1465⁰Å.

2.3 Discussion

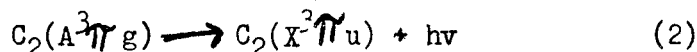
The fact that D₂ is observed as a product in the photolysis of C₂D₂ suggests that hydrogen is formed in a molecular elimination process since hydrogen atoms, if formed, would be removed by addition to acetylene rather than abstract to form molecular hydrogen. This is analagous to situation in the photolysis of ethylene. This could be checked in principle by photolysis of a mixture of C₂H₂ and C₂D₂, HD being taken as an indication of atomic reactions. As indicated, this is not feasible at low pressures required here due to contamination from water vapor. Addition of a known atom or radical scavenger (nitric oxide) fails to supress the formation of D₂ from C₂D₂. Since the observed emission is consistent with C₂ "Swan" bands ($A^3\Pi_g \rightarrow X^3\Pi_u$), both product analysis and spectral observations suggest the occurrence of the primary process



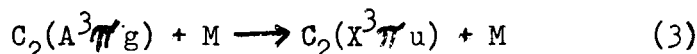
Process (1) is energetically possible at both the Kr line (1236⁰Å-231 k.cal) and the Xe line (1465⁰Å-195 k.cal). The fact that quantum yield for molecular hydrogen formation is 0.06 at both wavelengths indicates that (1) occurs to the same extent in each case. The intensity of the emission is greatly reduced however at the longer wavelength. Apparently, with the lower energy

of the Xe lines, most of the C_2 is not in the $^3\pi_g$ state but in low lying $^3\pi_u$ state or in ground $^1\Sigma_g^+$ state. Since the quantum yield for molecular hydrogen is low and the quantum yield of emission probably even lower, significant contribution from other primary processes is indicated.

The $C_2(A^3\pi_g)$ formed in (1) can lose energy by emitting light



or by collisional quenching



3 PHOTOLYSIS OF GASEOUS MIXTURES

3.1 Introduction

The photolysis of gaseous mixtures has been studied at the $1236\overset{\circ}{\text{A}}$ Kr line and emission spectra recorded in manner described in previous reports. The general purpose was to determine whether reactions such as



could be observed. Components of the mixture were chosen so as to supply diatomic molecules or radicals of cometary significance when exposed to ultraviolet radiation.

3.2 Results

Photolysis of $C_2H_2 - NO$ and $C_2H_2 - NH_3$ mixtures at total pressure of 100μ Hg results in observation of the violet system of CN in emission. The intensity of the emission increases with time. Initially no CN emission is detected, but it very quickly rises to become an extremely intense emission in the case of acetylene plus nitric oxide. At the same time, the characteristic " C_2 " emission from pure acetylene is greatly reduced in intensity. In the case of acetylene plus ammonia, the CN emission is much

weaker and changes less with time. The NH emission from ammonia and the C₂ emission from acetylene are only slightly reduced.

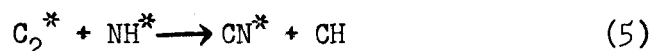
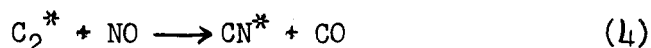
The violet system of CN has also been observed in photolysis of a mixture of carbon dioxide and nitric oxide. Again, the intensity of the emission is quite strong.

Photolysis of the following mixtures of gases does not result in the production of an emission not already observed in the original components:

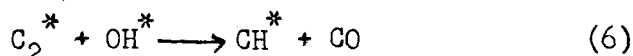
C₂H₂ + H₂O, C₂H₂ + CO, C₂H₂ + O₂, C₂H₂ + N₂, C₂H₂ + (CN)₂ and CO₂ + NH₃.

3.3 Discussion

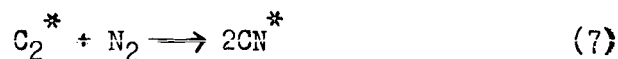
While it is tempting to ascribe the observation of CN emission in the photolysis of acetylene - nitric oxide mixtures and acetylene - ammonia mixtures to the occurrence of the reactions



it must be pointed out that many reactive fragments are present in the mixtures: C₂, possibly C₂H, H, C₂H₃ and C₂H₂^{*} from acetylene; N, O, NO^{*} and NO⁺ from nitric oxide; NH and NH₂ from ammonia. Reactions (4) and (5) as well as similar reactions, such as

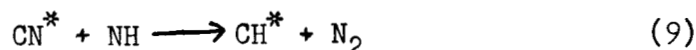


have been repeatedly suggested as being significant in the chemistry of flames. Based on negative results obtained in the photolysis of acetylene - water mixture and acetylene - nitrogen mixture, we may conclude that neither reaction (6) nor reaction (7)



are occurring under present experimental conditions. The possible occurrence

of reactions such as



could be checked by looking for NH emission in the photolysis of a mixture of cyanogen and water vapor and by looking for CH emission in photolysis of cyanogen and ammonia.

The occurrence or non-occurrence of reactions such as (5) through (9) at low pressures in the presence of vacuum ultraviolet radiation may be of considerable importance in deciding which stable compounds must be considered as part of a comet model.

4. Future Work

During the next quarter, the following will be prepared and submitted for publication:

- a. A full paper on various aspects of the vacuum ultraviolet photochemistry of acetylene.
- b. A note on the production of CN emission in the photolysis of mixtures of gases.
- c. A brief technical note on steps taken to improve intensity of vacuum ultraviolet resonance lamps.

It is expected that the study of the photolysis of water vapor and reactions of OH radicals begun late in this quarter will be actively pursued during all of the next quarter.

Work on electron bombardment of low temperature solids will be initiated in the next quarter. Preliminary experiments will commence in early July.

An attempt will be made to determine the radiative lifetime and hence the oscillator strength for the $A^3\Pi_g \rightarrow ^3\Pi_u$ transition of C_2 ("Swan bands") from the effect of pressure on the intensity of the observed C_2 emission in the photolysis of acetylene (reactions 2 and 3).